

PREPARATION OF Ti, Zr, Nb, AND Ta SOLID SOLUTIONS WITH Hf CARBIDE,
AND A STUDY OF THEIR PHYSICAL PROPERTIES

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PREPARATION OF Ti, Zr, Nb, AND Ta SOLID SOLUTIONS WITH Hf CARBIDE,
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Description of the procedure for preparation and of the physical properties of HfC-TiC, HfC-ZrC, HfC-NbC, and HfC-TaC solid solutions. Although these are less known than other carbide solid solutions, they are promising as ingredients for high-temperature alloys because of their high melting points. Preparation consists in the reduction of corresponding metallic oxides with carbon in an atmosphere of hydrogen or in vacuo, with or without simultaneous hot compression of reduction products. Physical properties of the carbides and those of the 18 prepared carbide compounds are tabulated. Curves of microhardness, specific thermal conductivity, thermal emf, heat conductivity, and Hall's constant vs variations in Hf carbide alloy composition are given. *Author*

The development of new branches of technology calls for alloys with a very ^{/180*} high melting point, reaching 4000°C. Alloys of the isomorphous carbides of transition metals of the IV and V groups on the periodic table of elements are the most promising in this respect, especially the mutual alloys of high-melting zirconium, hafnium, niobium and tantalum carbides.

As is well-known [1], alloys containing 80 mole % TaC and 20 mole % carbides of hafnium or zirconium have the highest melting points, 3942 and 3932°C respectively.

A number of works have been devoted to isomorphous carbide alloys [1-16], however, sufficient attention has not been paid to obtaining homogeneous alloys and investigating their physical properties in these studies. There are only data on X-ray investigations; the electrical resistance at room temperature and the microhardness of several carbide alloys were partially studied but practically no attention was given to the melting point and other physical characteristics.

*/The numbers in the margin indicate pagination of the original foreign text.

In this work, carbide systems in which there is unlimited mutual solubility were used as objects of study, because it is then much easier to trace the dependence of the physico-chemical properties on the alloy composition and to explain the reasons for this dependence.

In Figure 1, given in [4] and then supplemented in subsequent works [12, 16], the solubility of isomorphic carbides is graphically illustrated.

The carbides of metals of the IV and V groups of the periodic table are subject to the isomorphism rule, and they fulfill the necessary and adequate conditions of the formation of continuous series of solid solutions, formulated by I. I. Kornilov for intermetallic compounds [17] and later supplemented by the example of mutual boride alloys [18]. Consequently, unlimited solubility can be expected between them, within the group as well as between groups which, in fact, is justified in practice except for the VC-ZrC and HfC-VC systems in which, according to the data [4, 11], there is a limited solubility due to a large difference in the cell edges or dimensions of the carbides and the sizes of the atoms making up these metals.

The least studied alloys with hafnium carbide (HfC-TiC, HfC-ZrC, HfC-NbC and HfC-TaC), of considerable interest in the preparation of high-temperature alloys due to the high melting temperature of hafnium carbides (3890°C), were selected for investigation.

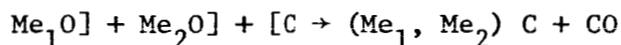
The Preparation of Solid Solutions of Carbides. The most prevalent method of obtaining solid solutions of carbides and other composite carbide alloys is their preparation from the individual carbides. However, as indicated in ref. 19, heating at a temperature of 2000°C for 20 hours in a hydrogen medium, pulverization and repeated sintering at high temperatures are necessary in this case to obtain homogeneous alloys. This process is technologically complex and

requires a good deal of time.

The conditions of obtaining solid solutions of carbides by the reduction of mixtures of oxides of the corresponding metals with carbon under various conditions -- in a hydrogen medium, in vacuum, and also by simultaneous heat pressing the reduction products in order to accelerate the homogenization of the carbide mixtures obtained in the reduction process, are studied in this investigation.

The process of the joint reduction of the oxides of the corresponding /181 metals with carbon should be considered to be more technological than preparation of the alloys by sintering the prepared carbides because the necessity for preparing the separate carbides previously is eliminated here and, in addition, the homogenization of mixtures of previously obtained carbides is a slow process due to the low chemical activity of carbides which are already formed.

Using the method of joint reduction of the oxides of the corresponding metals with carbon, the effect of the temperature and the passage time in vacuum and the hydrogen medium of the mixtures with a composition conforming to the following reaction



were studied.

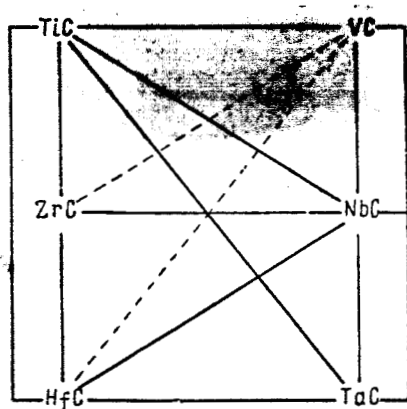


Figure 1. The solubility of carbides of metals of the IV and V groups of the periodic system of elements (according to data in ref. 12).

The oxides of titanium, zirconium, hafnium, niobium and tantalum, containing 99.37, 99.24, 99.34, 99.26 and 99.42% of the basic oxide respectively, were used in the study.

The obtained products were subjected to chemical analysis to determine the metal, total and free carbon content, and to an X-ray phase analysis. The completeness of the reaction was evaluated by the ratio A/B, the weight of the obtained product A to the weight of the composite carbide which should be formed when the proposed reaction goes to the end (B).

However, neither a three-hour passage time at 200°C in vacuum nor a one-hour passage time at 2500°C in a hydrogen medium are sufficient to assure obtaining a homogeneous solid solution of carbides; two systems of lines are observed in the radiograms of all products obtained.

Therefore, we investigated the method of reducing the oxide mixtures with carbon with simultaneous hot pressing [20] of the reduction products in order to activate and accelerate the homogenization of the carbide mixtures obtained in the reduction process.

It was assumed that this procedure would assure the obtaining of homogeneous alloys due to the closer contact of the carbide particles which are active immediately after reduction, and also due to the fact that the mutual diffusion of the components is accelerated as a result of the lowering of the activation energy of the process by applying external pressure in the form of hot pressing [20, 21] and the increase in defect mobility under these conditions.

Joint reduction of the mixtures of the corresponding metal oxides with carbon and with simultaneous hot pressing was carried out in graphite molds. The batch, which consists of a mixture of metallic oxides and carbon black, was placed in the mold and slowly (for 10 minutes) heated to a temperature of 1000°C,

then the pressing was carried out (the pressure on the powder was 180 kg/cm^2), followed by further heating to 2200°C during a 5 minute period of time; the passage time at this temperature was also 5 minutes.

The radiograms of the products obtained by the reduction of oxide mix- /182 tures with carbon in vacuum, a hydrogen medium and under conditions of reduction and simultaneous hot pressing and the radiograms of products obtained in vacuum and in a hydrogen medium and then subjected to hot pressing, are given in Figure 2.

It is evident from these data that the reduction products subjected to hot pressing are homogeneous solid solutions of carbides (there is only one system of lines on the radiograms), which indicates the activating role of pressure on the powder in the sintering and homogenization process.

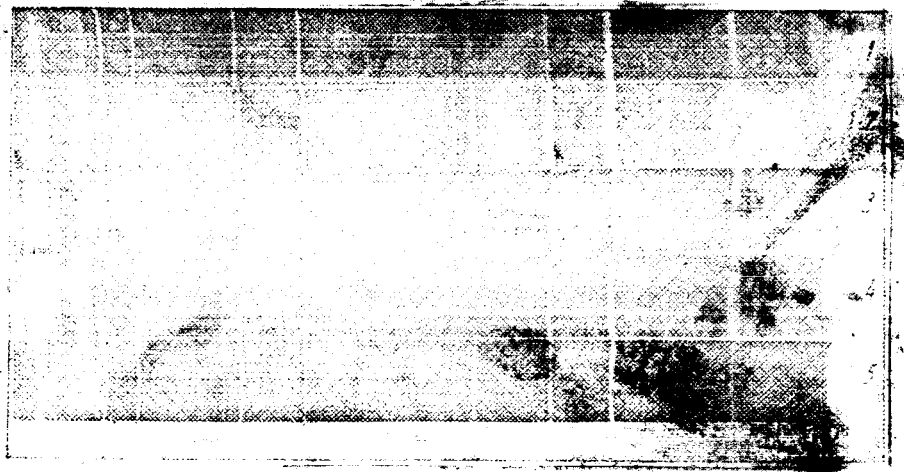


Figure 2. The radiograms of products obtained in the joint reduction of oxides with carbon under various conditions: 1. in vacuum; 2. in a hydrogen medium; 3. by reducing oxide mixtures with carbon accompanied by simultaneous hot pressing; 4. in vacuum with subsequent hot pressing; 5. in a hydrogen medium with subsequent hot pressing.

The specimens obtained by joint reduction of the oxides with carbon and with simultaneous hot pressing of the reduction products have a high porosity

(up to 25%) due to the intense evolution of gas in the reaction process. The obtained products are homogeneous solid solutions of the corresponding carbides.

Thus, the proposed method assures the obtaining of homogeneous alloys of isomorphous carbides in a comparatively short period of time (about 0.5 hours).

Preparation of Compact Specimens of Carbide Alloys and Measurement of the Physical Properties. The specimens used in the investigation of the physical properties of carbide alloys were prepared by sintering, using the method of hot pressing of the products obtained by the joint reduction of oxides with carbon and simultaneous hot pressing. The porous products obtained received a preliminary pulverization in an Abikh mortar, were screened through a sieve with a coarseness of 40 μ m and subjected to magnetic separation. Sintering was carried out within the temperature range 2500-2700°C for 5 minutes under a pressure of $\sim 300 \text{ kg/cm}^2$. The residual porosity of the specimens obtained by this procedure was 5-7%.

In order to remove internal stresses, the specimens were annealed in vacuum at a temperature of 2000°C for 4 hours and subsequently cooled slowly at a rate of 10 degrees per minute.

The obtained specimens were analyzed in the same manner as the powders. /184 Chemical analysis revealed a general absence (in individual cases, however, no more than 0.05%) of free carbon and a conformity of content ratios and totals of the metals and carbon to the stoichiometric formulas of the investigated alloys.

The specimens used in measuring the melting point, the microhardness and the coefficient of thermal expansion were 8 mm in diameter and 12-15 mm long; the thermo-e.m.f., specific electrical resistance, thermal conductivity, susceptibility and the Hall coefficient measurements were carried out on specimens in the form of parallelepipeds with dimensions of 12 x 2.5 x 0.6 mm. In this case,

all the identical properties were measured on the same specimen.

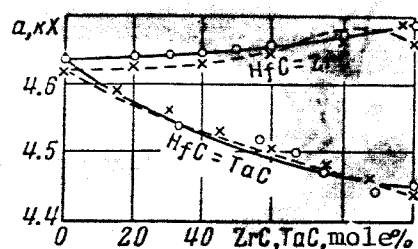


Figure 3. The dependence of crystalline cell edges on the composition of HfC-ZrC and HfC-TaC alloys; our data is represented by solid lines and the data from refs. 10 and 11 by dashed lines.

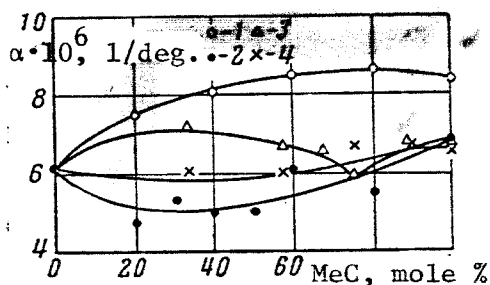


Figure 4. The dependence of the coefficient of thermal expansion on the composition of HfC alloys with TiC (1), ZrC (2), TaC (3) and NbC (4).

Data on the concentration dependence of the physical properties of isomorphous carbide alloys are given in Table 1.

According to the data from metallographic and X-ray studies, the obtained alloys are homogeneous and form continuous series of solid solutions in the investigated carbide systems.

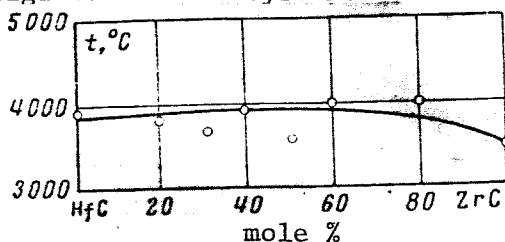


Figure 5. The dependence of the melting point on the composition of alloys in the HfC-ZrC system.

Table 1. Physical Properties of the Carbides and Their Compounds

Состав сплава, мол. %			Состав сплава по анализу, %		a, X	$\alpha \cdot 10^4$ 1/град	$t_{пл}, ^\circ C$	H_D кг/мм ²	ρ , г/см ³	$\lambda \cdot 10^4$ кал/см ² · град	$-E$, мкв/град	$-R \cdot 10^4$ см ² /кул	$\kappa \cdot 10^4$ (моларн.)	Работа выхода эл., эв	Коэффициент излучения ($\lambda = 655$ микрон) 1700° C
TiC	ZrC	HfC	б, вес. %	Me											
100	—	—	20.12	79.9	4.315	7.74	3147	3000	52.5	88.0	12.6	6.7	+5.70	2.35	0.90
100	100	—	11.67	88.4	4.679	6.73	3530	2600	50.0	49.0	12.7	9.4	-23.00	3.80	0.76
—	—	100	6.34	93.7	4.635	6.59	3890	2600	45.0	62.2	12.5	12.4	-25.50	2.04	0.77
—	—	—	11.45	88.5	4.460	6.65	3480	1961	51.1	55.0	5.4	1.3	+15.30	2.24	0.85
—	—	100	6.30	93.7	4.417	8.29	3880	1599	42.4	34.7	6.6	1.1	+9.30	3.14	0.85
80	—	20	14.02	85.9	—	8.56	—	4000	49.5	55.4	7.4	7.5	—	—	—
60	—	40	10.77	89.3	—	8.42	—	4250	56.3	41.0	6.8	7.6	—	—	—
40	—	60	8.72	91.3	—	8.21	—	4600	54.5	45.9	7.4	8.9	—	—	—
20	—	80	7.29	92.7	—	7.50	—	3300	43.5	55.6	8.3	7.9	—	—	—
—	80	20	10.02	90.0	4.672	5.42	3975 ± 150	2850	43.7	40.9	10.8	8.2	+5.96	—	—
—	60	40	8.71	91.3	4.654	6.10	4000 ± 150	2600	44.7	48.1	10.4	9.8	+10.90	—	—
—	50	50	8.21	91.8	4.651	4.94	3540 ± 150	2200	41.9	47.8	9.6	9.8	+10.92	—	—
—	40	60	7.75	92.2	4.644	5.00	3900 ± 100	2850	45.8	43.2	11.3	11.8	—	—	0.91
—	30	70	7.32	92.7	4.642	5.33	3570 ± 150	3000	45.5	42.0	11.6	11.2	+18.82	—	—
—	20	80	7.00	92.9	4.641	4.73	3700 ± 150	2850	44.0	62.6	10.2	3.9	+14.21	—	—
—	—	11	10.54	89.5	—	6.48	—	2850	47.9	36.2	6.9	4.4	—	3.96	—
—	25	75	9.62	90.5	—	6.32	—	2600	50.6	31.6	5.9	4.7	—	—	—
—	43	57	8.50	91.5	—	6.11	—	2850	77.5	28.7	6.6	3.3	—	4.11	—
—	—	33	7.43	92.6	—	6.08	—	2850	65.5	42.8	7.5	5.2	—	4.12	—
—	89	11	6.25	93.7	4.443	6.57	4050 ± 50	2600	50.0	60.6	6.0	1.5	—	—	—
—	75	25	6.26	93.7	4.476	5.82	—	2600	33.9	142.0	4.1	1.1	—	—	—
—	67	33	6.26	93.7	4.500	6.54	—	2350	61.6	31.8	6.3	4.0	—	—	—
—	—	—	6.27	93.7	4.538	7.50	—	2850	54.1	39.8	8.0	8.0	—	4.12	0.62

- a. Alloy composition, mole %
b. Alloy composition according to chemical analysis, % by weight ($C_{tot.}, Me$)
c. $a \cdot 10^6$, 1/deg.
d. Melting point, °C
e. H_D , kg/mm²
f. ρ , microhm · cm
g. $\lambda \cdot 10^3$, cal/cm · sec · deg
h. $-E$, microvolt/deg
i. $-R \cdot 10^4$, cm³/coulomb
j. $\kappa \cdot 10^6$ (molar)
k. Electron work function (eV)
l. Coefficient of radiation ($\lambda = 655$ mμ), 1700°C

The variation curves of the crystalline cell edges of the alloys in the HfC-ZrC and HfC-TaC systems (Figure 3) have a form characteristic for a continuous series of solid solutions and are somewhat deflected from additivity to the negative side. This serves to confirm a strengthening of interatomic interaction in the solid solution systems as compared with the individual carbides.

The data obtained in this work are in good agreement with the data in refs. 10 and 11, although the deflection in the curve of cell edge dependence on the composition is not observed in the HfC-ZrC system; this should represent the truth more accurately than the data in refs. 10 and 11 because, according to the results of numerous physical property measurements in this system, a continuous series of solid solutions exists.

The coefficient of thermal expansion in the alloys of the HfC-NbC and HfC-ZrC systems is somewhat lower than in the individual carbides (Figure 4). This testifies to a strengthening of the inter-atomic bond. The coefficient of thermal expansion minimum in the HfC-TaC system invites particular attention. As is known, the melting point maximum corresponds to it. /185

Preliminary measurement of the melting points of the alloys showed an elevation of the melting point as compared with the original components. Thus, the melting point of an alloy containing 80 mole % TaC and 20 mole % HfC, according to our data, is $4050 \pm 50^{\circ}\text{C}$. This somewhat exceeds the value obtained in ref. 1. An insignificant rise in the melting point is also observed in the HfC-ZrC system (Figure 5).

Earlier, it was shown in ref. 22 that the relative height of the microhardness maximum in continuous series of solid solutions increases with increasing diversity of acceptor ability of the atoms of the transition metals* entering

*The acceptor ability is evaluated by the expression $1/Nn$, proposed in ref. 23,

where n is the number of electrons in the d-shell of the single atom and N is the principal quantum number of the d-level.

into the composition of the corresponding compounds (carbides, nitrides, borides, etc.). As is evident from Figure 6a and Table 2, the greatest hardness corresponds to the greatest diversity of acceptor ability criteria values of titanium and hafnium, even as in this case.

Table 2

Acceptor Ability and Electron Structure of Transition Metal Atoms

Metal	$1/Nn$	Electron configurations of the outer shells	System	Diversity Δ of $1/Nn$ values
Ti	0.167	$3d^2 4s^2$	TiC-HfC	0.067
Zr	0.125	$4d^2 5s^2$	ZrC-HfC	0.025
Hf	0.100	$5d^2 6s^2$	TaC-HfC	0.033
Ta	0.067	$5d^3 6s^2$	NbC-HfC	0.037
Nb	0.063	$4d^4 6s^1$		

The lesser hardness corresponds to a diversity of $1/Nn$ values, $\Delta = 0.033 - 0.037$, while in the ZrC-HfC system with $\Delta = 0.025$, an alloy of equimolar composition not only has the least hardness but is characterized in general by a sharply expressed microhardness minimum which is unusual for systems with continuous series of solid solutions. Such a sharp minimum is probably found also in connection with the structural characteristics of the metallic system Hf-Zr in which, with 35-50 mole % Zr, there is a melting point minimum [24] apparently associated with the decrease in the concentration of the bonding electrons. This, in turn, is the result of a small difference Δ between the Hf and Zr atoms which brings about a small exchange of electrons between these atoms when alloys with a composition approaching equimolar are formed. This thermodynamic equi-

librium is destroyed when any of the components have an excess of atoms, while the phase itself, formed during equilibrium, corresponding to a minimum of bonding electron concentration, evidently should have the features of a chemical individual similar to superlattices. The electron density distribution in carbides is analogous to that in metals, therefore, their solid solutions should have similar characteristics of some properties, as is the case in the ZrC-HfC system where known features of a chemical individual also can be attributed to an equimolar composition.

The character of hardness variation in the TaC-HfC and NbC-HfC systems /186 indicates that the addition of HfC to these carbides at first causes a substantial increase in the hardness, up to the level of HfC hardness, but when the HfC content exceeds 10%, the increase in hardness practically ceases. In other words, the hardness increases at first due to the formation of exchange bonds between Hf, on the one hand, and Nb or Ta, on the other; then, as the HfC content is increased, the role of this exchange in the determination of bond stability becomes insignificant and a peculiar type of saturation ensues, in which the hardness is determined mainly by the bonds characteristic for hafnium carbide.

On the other hand, an increase in the resistance maximum level with decreasing diversity Δ is generally characteristic for the electrical resistance (Figure 6b), evidently due to the lesser probability of sd-exchange between metallic atoms which is equivalent to a lesser probability of filling the d-electron shells and an increase in their acceptor or dispersing ability with respect to the conducting electrons [25]. The sharp electrical resistance minimum in the HfC-TaC system when the HfC content is about 25 mole %, corresponding to a melting point maximum and thermal expansion coefficient minimum, invites atten-

tion.

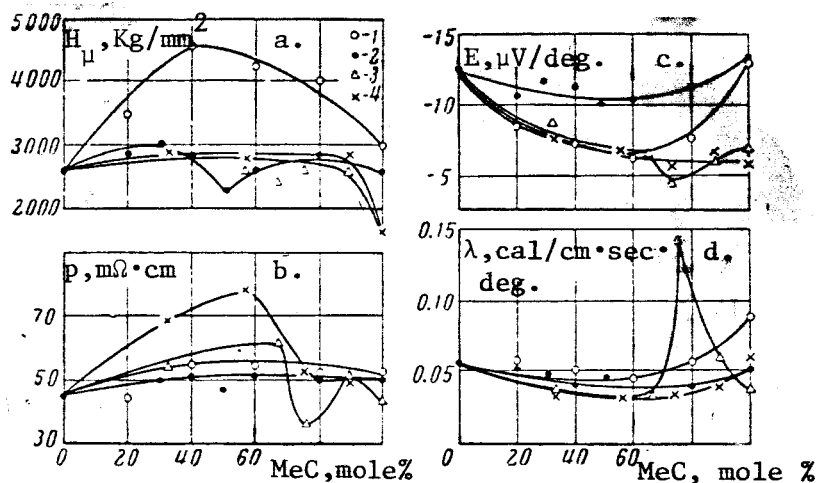


Figure 6. The dependence of the microhardness (a), the specific electrical resistance (b), the thermoe.m.f. (c) and the thermal conductivity (d) on the composition of HfC alloys with TiC (1), ZrC (2), TaC (3) and NbC (4).

By examining the electron configuration of metallic atoms (Table 2), we can conclude that it is possible only in the TaC-HfC system to have the formation by hafnium and tantalum atoms of a stable $5d^5$ electron configuration which, due to the proximity of the atomic weights of Ta and Hf, should almost correspond to an equimolar alloy of carbides and, apparently be displaced in the direction of a large tantalum carbide content under the influence of the carbon atoms, the p-electrons of which are capable of filling the d-shell of the atoms of strongly accepting hafnium to a greater degree than with tantalum. Therefore, a greater tantalum atom content is necessary in the alloy than hafnium in order to achieve the $5d^5$ configuration.

The study carried out by O. I. Shulishova on the superconductivity of solid solutions of carbides, one of the components of which was hafnium carbide, showed that, with a reduction of the acceptor ability of the metal, the

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carbide of which dissolves in hafnium carbide (i.e., with an increase in Δ), an increase in the sd-exchange interaction between the metallic atoms and a strengthening of the lattice, which causes an increase in the values of the points of transition to superconductivity (T_k), occur.

<u>System</u>	<u>$T_k, ^\circ K$</u>
HfC-TiC	1.38
HfC-ZrC	1.38-1.68
HfC-NbC	6.0-7.5
HfC-TaC	7.3-7.9

Here, the highest T_k value again corresponds to the alloy containing ~ 80 mole % TaC and ~ 20 mole % HfC.

The extremes of the properties for this alloy can also be seen in the thermo-e.m.f. curves (Figure 6c) and the thermal conductivity curves (Figure 6d). The latter is particularly important and is of interest because it indicates that the formation of a d^5 -type configuration sharply limits the possibility of lattice vibrations and photon scattering.

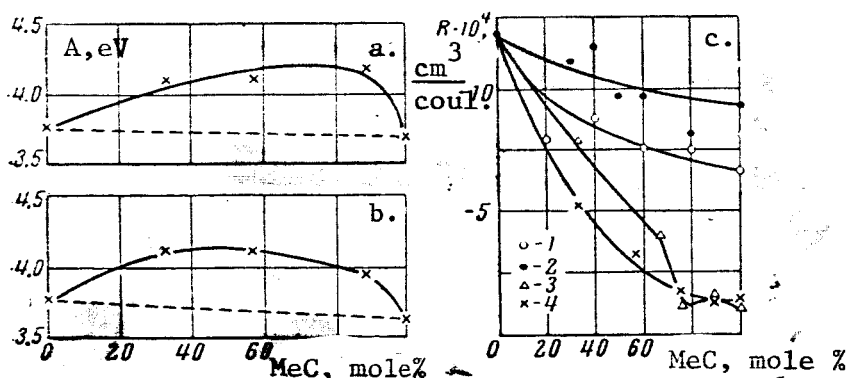


Figure 7. The work function during thermal emission as a function of the composition of HfC-TaC (a) and HfC-NbC (b) alloys.

Figure 8. The Hall coefficient as a function of the composition of HfC alloys with TiC (1), ZrC (2), TaC (3) and NbC (4).

When the degree of filling of the d-level is increased due to sd-exchange between the atoms of the metals Me_1 and Me_2 entering into solid solutions of carbides, the work function of the electrons during thermal emission increases whereby the largest electron work function values correspond to the formation of the most stable electron configurations (Figure 7), e.g., in the TaC-HfC system, the work function maximum corresponds to an alloy with a probable formation of a d^5 configuration which is very difficult to destroy during thermal emission excitation. The tendency to destroy the monotony of the Hall coefficient variation curve again takes place for the TaC-HfC system with 80 mole % TaC (Figure 8).

It should be noted that the nature of change in the physical properties of solid solutions of carbides is determined by the relationship of the acceptor capability of the atoms of the metals and the probability of forming stable d^5 -type electron configurations.

In conclusion, the authors wish to express their thanks to S. N. Lvov and V. S. Fomenko for carrying out the investigations on a number of physical properties and to Yu. B. Kuzma who performed a good part of the radiographic studies on solid solution of carbides.

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